

# CHARACTERIZATION OF TOXIC GASEOUS EMISSIONS FROM INDUSTRIAL SOLID WASTE LANDFILLS

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**SUMMARY:** In France, Hazardous Industrial Waste, once stabilized, are buried in specific landfills. As for all polluting activities, these facilities must report to the EPER Register their toxic gaseous emissions, expressed in mass per year, as soon as they exceed threshold limit values. Campaigns were conducted on two different hazardous waste landfills in order to establish if these facilities needed to report to EPER Register. Global fluxes of gaseous components were measured by means of an FID (hydrocarbons) and a PID (halocarbons, aromatics and some non-organic compounds). Specific concentrations of aromatic (BTEX) and chlorinated hydrocarbons were also measured. Gaseous emissions were generally very low. Emissions were only detected for young and medium-aged layers, between 1 day and 3 months old. Due to these low emissions, and to the small surfaces involved, the two landfills do not fall under the EPER emission Register.

## 1. INTRODUCTION

In France, Hazardous Industrial Waste, once stabilized, are buried in specific landfills. As for all polluting activities, these facilities must report to the EPER Register their toxic gaseous emissions, expressed in mass per year, as soon as they exceed threshold limit values. A lot of compounds can be emitted by industrial waste. Depending on the type and age of waste, type and concentration of gaseous emissions can be very different, which would take a lot of time and money to characterize. Therefore, the study was limited to a few gases, which are good tracers for risks assessment : VOC, and among them, BTEX and chlorinated compounds. The aim of this study was to establish the fugitive VOC emission of two industrial waste landfills, representative of the French sites. The sites measurements were of two kinds :

- total gaseous emissions measured with a static flux chamber, on different parts of the landfills, in order to evaluate the participation of parts of different ages to the global emissions,
- b) VOC sampling and identification in order to calculate toxic gases fluxes to be reported to EPER (benzene, toluene, xylenes, halogenated compounds).

## 2. EXPERIMENTAL STUDY

### 2.1 Materials and methods

#### 2.1.1 Fluxes measurements

Fluxes of total hydrocarbons + aromatic and chlorinated compounds were measured through a static flux chamber (Savanne et al, 1997) equipped with flame ionisation and photo-ionisation detectors. Measurements were performed every 5 to 20 meters, depending on the surface area to be explored. A minimum of 10 points were analysed on the smallest zones. The flux chamber (INERIS patented) covers a surface of 0.25 m<sup>2</sup>. The minimum flux detected by this method is 0.01 ml/m<sup>2</sup>/min, and the precision of the method is 0.05 ml/m<sup>2</sup>/min. This chamber is generally used for exploring surface methane emissions on MSW landfills.

The flame ionisation detector used with this chamber is non-selective and responds to all hydrocarbons. On MSW landfills, surface emissions consist mainly in methane, which is not the case here. In order to improve the selectivity of the method, a photo-ionisation detector, which responds to lesser gases, was added to determine mainly aromatic hydrocarbons, halocarbons, hydrocarbons with double or triple bonds, and some inorganic gases like ammonia.

The flame ionisation detector is calibrated with methane, compound which gives the smaller response to the FID. The major organic compounds identified on the two sites, analysed by gas chromatography/mass spectrometry, are hydrocarbons with 5 to 8 atoms of carbons. FID measurements were corrected to give fluxes in equivalent-pentane, compound which gives the higher – and therefore the worst - values for the total flux.

The photo-ionisation detector is calibrated with iso-butylene. Other compounds give response which can be either bigger or smaller than iso-butylene, therefore no correction was made.

#### 2.1.2 VOC identification and measurement

To quantify toxic gases, soil gases were sampled on each zone which was studied, except the ones with no surface fluxes. Sampling was done in evacuated canisters (US EPA TO14A, TO15) in order to quantify benzene, toluene, xylenes, vinyl chloride, tri- and tetrachlorethene by gas chromatography/flame ionisation detector. Sampling was performed on the flux chamber, at the end of a flux measurement, and monitored by either the FID or PID (Figure 1).

In addition, on each site, two samples of surface gases were taken on different zones. These samples on adsorption tubes were analysed by thermal desorption/gas chromatography/mass spectrometry, in order to identify the major VOC.

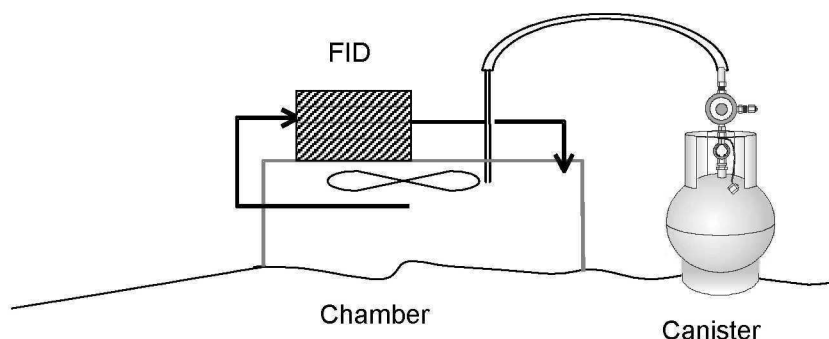


Figure 1. Gas sampling for VOC analysis on the flux chamber

## 2.2 Sites description

Depending on the site, hazardous waste which are landfilled are mainly constituted of:

- dispersed waste which is stabilized with cement-type material, such as MSW incinerator fly ashes,
- stable waste like mineral oxides,
- dispersed waste, such as asbestos, contained in large bags.

Large bags are only deposited on site 1. On site 2, only stable or stabilized waste are deposited.

Landfills are organised in partial compact layers, approximately 1.5 meters high, 2-10 m large, up to 50 m long, which represent one day of disposal. These daily disposals are made one beside the other, for up to one month. Then, another layer is started over the top of this arrangement. Large bags layers are sometimes covered by a thin layer of soil which was previously bioremediated on-site. The surface covered by each layer is not large, but the total height of the disposal can be high, up to 20 meters and more above the ground. Once completed, the section is covered with a geomembrane and a 1 meter-thick layer of clay.

Partial layers of wastes of different ages were investigated separately: from 1-2 days, up to 2-3 years old.

## 3. RESULTS AND DISCUSSION

### 3.1 Recent layers (2-8 days)

Due to the deposition process (engine movements) and the unsteadiness of new layers, it was not possible to make fluxes measurements over layers less than 2 days old. Nevertheless, fluxes of hydrocarbons measured by the FID over this type of layers were very low (Table 1).

Fluxes measured by the PID are smaller than those with the FID on site 1, which means that gaseous fluxes are constituted of hydrocarbons. It is not the case on site 2 : response are higher on the PID than on the FID. The number of organic compounds which respond to the PID being smaller than on the FID, the larger signal on the PID probably originates from the measurement of inorganic compounds like ammonia or nitric oxides. These fluxes remain small compared to surface emissions of biogas on certain MSW landfills.

Recent layers represent a small area, where fluxes are low. Therefore, total fluxes over these areas are limited, though fluxes of possible inorganic gases are measured over site 2.

BTEX and halogenated compounds concentrations were analysed on samples taken in the flux chamber, at the end of fluxes measurements over young layers, for the 2 sites. Results are given in Table 2.

Table 1. Gaseous fluxes measured on recent disposal zones

	Age of layer	Mean fluxes, ml/m <sup>2</sup> /min		Surface area, m <sup>2</sup>	Total fluxes, ml/min	
		FID	PID		eq. pentane	eq. iso-butylene
Site 1	2 days	0.06	0	100	5.6	0
	2 days	0.07	0.04	50	3.5	1.8
Site 2	2 – 8 days	0.03	0.8	150	2	120
	2 days	0.01	4.8	48	0.6	230

Table 2. Gas analysis for recent disposal zones

Concentrations, $\mu\text{g}/\text{m}^3$	Site 1		Site 2	
Benzene	ND*	ND	ND	4.70
Trichlorethene	4.23	1.88	ND	ND
Toluene	1.72	<QL**	ND	1.47
Tetrachlorethene	ND	ND	ND	ND
Ethylbenzene	0.69	0.70	ND	ND
m+p Xylene	1.20	1.67	ND	1.77
o-Xylene	ND	1.11	ND	3.55
Vinyl chloride	ND	ND	ND	ND

\* ND: not detected, \*\* QL: quantification limit

On the soil gases samples taken in the flux chamber after flux measurements, concentrations of the target compounds are very low, and comparable to the values measured in ambient air (Zdanevitch *et al*, 2006). Benzene is only detected on one sample on site 2, at a concentration which is below the European Limit Value to be attained in 2010 in ambient air ( $5 \mu\text{g}/\text{m}^3$  : EC Directive, 2000). Trichlorethene is only encountered on site 1, but on the two samples. No tetrachlorethene and no vinyl chloride are detected on any sample.

### 3.2 Medium-aged layers (15 days – 1 month)

On site 1, two zones which were 1-month old were attainable. On site 2 there was only one medium-aged zone. The age of the waste disposal vary from one part of the layer to the other part, from 3 months to a few days. This layer is also constituted of two parts : one with only stabilized waste (on the left on Figure 2), the other is a mix between stable and stabilized waste. Results of the flux measurements are given in Table 3. Analysis of soil gases sampled at the end of flux measurements are given in Table 4.

On site 1, emissions from the two 1-month old zones are similar. Fluxes measured by the PID are a little higher (5 to 10 times) than those measured by the FID. This behaviour can come from hydrocarbons which give a higher response on the PID than on the FID, or from the presence of compounds which do not give a response to the FID, like inorganic compounds. Nevertheless, emissions are so low that it is difficult to determine the origin of the signal. However, we have sampled the soil gases on the flux chamber to characterize the presence of VOC.

On site 2, fluxes measured by the PID are higher than values determined by the FID, but there is a different behaviour on stable and stabilized waste (Figure 2). FID values are generally similar to PID values on stable waste, though PID values are more dispersed, probably because the limit of detection and response time are better on the FID. On stabilized waste (with cement-like material), PID values are generally higher than FID values. This may be due to the presence of either inorganic compounds or organic compounds with a higher response to the PID. On this zone, the higher values of flux corresponds to fractures of the surface. Mean flux values are still low, but the surface of this zone is larger than the younger ones, so the total flux for this zone is a little more important, though still below 1 litre/min.

Table 3. Gaseous fluxes measured over medium-age disposal zones

	Age of layer	Mean fluxes, ml/m <sup>2</sup> /min		Surface area, m <sup>2</sup>	Total fluxes, ml/min	
		FID	PID		eq. pentane	eq. iso-butylene
Site 1	1 month	0.001	0.006	1350	1.35	8
	1 month	0.002	0.03	375	0.8	11.3
Site 2	1 – 3 months	0.15	0.43	1420	213	610

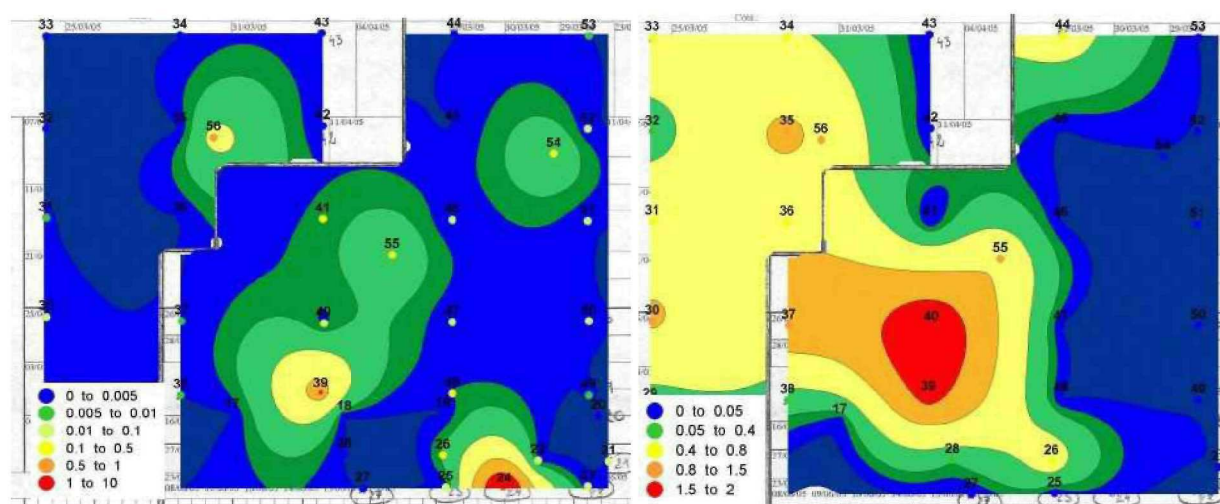


Figure 2. Interpolation of gas fluxes measured by : FID (left) and PID (right). Site 2, zone aged 1 to 3 months

Table 4. Gas analysis for medium-age disposal zones

Concentrations, $\mu\text{g}/\text{m}^3$	Site 1		Site 2	
Benzene	<QL**	5.19	<QL**	3.51
Trichlorethene	2.44	15.79	ND*	ND
Toluene	3.02	8.81	<QL*	ND
Tetrachlorethene	35.17	56.11	ND	ND
Ethylbenzene	1.46	8.26	ND	ND
m+p Xylene	2.07	8.66	1.11	ND
o-Xylene	1.99	11.33	1.76	ND
Vinyl chloride	ND*	ND*	ND*	5.13

\* ND: not detected, \*\* QL: quantification limit

On 1-month old layers, several sampling points show emissions below quantification limits of the FID and PID. Nevertheless, BTEX and chlorinated compounds were sometimes detected in the canisters samples, but with concentrations not much higher than those of a typical urban air, except for the chlorinated compounds.

Tetrachlorethene is the only compound measured with a slightly higher value, and only on site 1, but on both samples taken on two different zones. This corresponds to a higher value also for trichlorethene, on one sample.

On site 2, only 2 compounds are quantified on each sample. Xylenes are present on one

sample, taken on a 1-month deposit, and benzene and vinyl chloride are measured on the sample taken on a 2-month deposit. The higher response of the PID cannot be explained on site 2 by the presence of aromatic or chlorinated hydrocarbons. It is more probable than this response is due to inorganic compounds, which were not searched specifically.

### 3.3 Old layers (6 months – 1 year)

For site 1, only one old zone could be explored : this zone is more than 2 years old, and has been rehabilitated with a geomembrane, covered by a thick layer of clay, soil and grass.

On site 2, the two older zones were respectively 4 to 6 and 6 to 8 months old and made of stabilized waste. The surface of the younger zone is very dry and dusty.

Values of fluxes measured over these zones are given in Table 5. Analysis of one soil gas sample for site 2 is given in Table 6.

On site 1, no emissions were measured over the rehabilitated zone: all fluxes were null.

On site 2, the two zones show a slightly different behaviour. The younger zone show no emission, though the older zone show a small mean flux on the PID values. The surface of this zone is rather small, so the total flux is very low. Nevertheless, soil gas was sampled in a canister (Table 6).

On the older zone of site 2, which show a very low flux on the FID (but not on the PID), some aromatic and chlorinated compounds are present: all the xylenes and vinyl chloride. Their concentrations are as low as the ones usually measured in ambient air. The presence of these compounds can be linked to the fluxes measured, though the concentrations are too low to explain the PID response.

Table 5. Gaseous fluxes measured over old disposal zones

	Age of layer	Mean fluxes, ml/m <sup>2</sup> /min		Surface, m <sup>2</sup>	Total fluxes, ml/min	
		FID	PID		eq. pentane	eq. iso-butylene
Site 1	> 2 years, rehabilitated	0	0	4000	0	0
Site 2	4 – 6 months	0	0	1080	0	0
	6 – 8 months	0	0.18	400	0	70

Table 6. Soil gas analysis for old disposal zones

Concentrations, µg/m <sup>3</sup>	Site 2
Benzene	ND*
Trichlorethene	ND
Toluene	ND
Tetrachlorethene	ND
Ethylbenzene	ND
m+p Xylene	3.97
o-Xylene	2.77
Vinyl chloride	5.30

\* ND: not detected

### 3.4 Large bags

Large bags are only deposited on site 1. Large bags are deposited in layers: the deposition of a layer takes several days. When a layer is more or less full, a temporary cover, made of contaminated soil which is biologically treated on site, is deposited on the top. Older layers are covered by a thick layer of clay. No measurement was possible directly on the large bags, so the younger zone with temporary cover and the older zone with clay cover were explored. Results of flux measurements are presented in Table 7. Soil gases were also sampled in canisters at the end of a flux measurement on each zone: results are given in Table 8.

Most points of the recent zone show hydrocarbons fluxes measured by the FID. Only some of those points show a response on the PID. It may be concluded that the measured gases are probably a mixture of hydrocarbons containing a part of alkanes, which do not respond to the PID. Sampling of soil gas was made in order to verify this point. There are also points on this zone where emissions are null. Therefore mean fluxes are small. As the surface of this zone is small, emissions due to this deposition are still very low.

On the old aged large bags zone, which is covered by a layer of clay, only a few points showed very small fluxes, in the order of magnitude of the smaller flux detected. Therefore, the mean flux for this zone is close to zero.

On the recent large bags zone, for the soil gas sample, all target compounds are present except vinyl chloride, and in higher concentrations than those found in ambient air (Zdanévitch *et al*, 2006). The most abundant compounds are the chlorinated ones, showing the presence of residues of solvents. These emissions can come either from the waste disposed in the large bags, or from the soil used as a temporary cover, which has undergone a biological treatment on the site. Though values seem to be high, they are still low compared to those measured during fluxes measurement: they are in the high ppbv range, when flux measurements are in the ppmv range. As a consequence, the flux measured by the PID on this point is null, since the sum of the gas concentrations (BTEX and chlorinated) is below the PID detection limit.

Table 7 : gaseous fluxes measured over large bags disposal zones

	Age of layer	Mean fluxes, ml/m <sup>2</sup> /min		Surface area, m <sup>2</sup>	Total fluxes, ml/min	
		FID	PID		eq. pentane	eq. iso-butylene
Site 1	Recent	0.05	0.03	270	13.2	8.4
	Old	0	0	500	0	0

Table 8 : gas analysis for large bags disposal zones

Concentrations, $\mu\text{g}/\text{m}^3$	Site 1	
	Recent	Old
Benzene	71.54	ND*
Trichlorethene	816.88	ND
Toluene	139.51	<QL**
Tetrachlorethene	219.57	ND
Ethylbenzene	64.00	ND
m+p Xylene	49.28	ND
o-Xylene	37.60	ND
Vinyl chloride	ND	ND

\* ND: not detected, \*\* QL: quantification limit

On the old aged zone, though the sample was taken on a point where the flux was not null, no target compounds are measured in the soil gas. Only toluene is detected, but it stands below quantification limits. Other compounds are not detected by the method.

#### **4. CONCLUSIONS**

The gaseous surface emissions of two industrial dangerous waste landfills in France were studied, by two means of measurements : FID analyser which responds to all hydrocarbons, and PID which respond to less hydrocarbons (alcene, aromatic, chlorinated...) and to inorganic gases such as nitrous oxides and ammonia. The measured emissions were generally low, and as could be expected, were higher on recent disposal zones than on older ones. Differences between the spatial distribution of the FID and PID values were identified, depending on the nature of the waste.

Aromatic and chlorinated toxic compounds have been quantified on soil gas samples taken on the flux chamber. Though they were often present on the samples, their concentrations were usually very low, and comparable to those found in ambient air. These concentrations do not explain totally the fluxes measured on the PID analyser. Therefore, some inorganic compounds, which were not specifically searched, should be present. Relatively high hydrocarbon concentrations were only reported on the big bags recent zone, which is covered by a layer of biotreated soil.

Due to low mean fluxes, very low concentrations of toxic VOC and to the small areas of the sites, total emissions of those sites are low enough, and the sites do not have to report their emissions to the EPER register.

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